SAMSO-TR-68-468

4μ BAND RADIATION FROM HIGH TEMPERATURE AIR

K. L. Wray and R. L. Taylor

AVCO EVERETT RESEARCH LABORATORY

RESEARCH REPORT 322
JANUARY 1969

jointly sponsored by
ADVANCED RESEARCH PROJECTS AGENCY
DEPARTMENT OF DEFENSE
ARPA Order No. 1092
and
SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
DEPUTY FOR RE-ENTRY SYSTEMS (SMY)
Norton Air Force Base, California 92409

SAMSO-TR-68-468 RESEARCH REPORT 322

4 μ BAND RADIATION FROM HIGH TEMPERATURE AIR*†

by

K. L. Wray and R. L. Taylor

January 1969

AVCO EVERETT RESEARCH LABORATORY
a division of
AVCO CORPORATION
Everett, Massachusetts

*This research was supported by the Advanced Research Projects Agency of the Department of Defense and Space and Missile Systems Organization, Air Force Systems Command and was monitored by Space and Missile Systems Organization, Air Force Systems Command under Contract F04701-68-C-0036.

† Being submitted to J. Q. S. R. T.

FOREWORD

Distribution of this document is unlimited. This indicates document has been cleared for public release by competent authority.

"This research was supported by the Advanced Research Projects Agency of the Department of Defense and Space and Missile Systems Organization, Air Force Systems Command and was monitored by Space and Missile Systems Organization, Air Force Systems Command under Contract F04701-68-C-0036." The secondary report number as assigned by AERL is Avco Everett Research Laboratory Research Report 322. The Air Force program monitor for this contract is T. W. Graham, 2nd Lt., USAF, Project Officer, Environmental Technology Branch, SMYSE.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions; it is published only for the exchange and stimulation of ideas.

T. W. Graham, 2nd Lt., USAF,
Project Officer,
Environmental Technology Branch
SMYSE

ABSTRACT

Experimental measurements are reported on high temperature air and other gases to establish the source of a band of radiation observed at 4.0 μ. Both a 1 atm arc jet and a shock tube were used to provide a temperature range of 5400-8000°K in air. Experiments established that the radiation was not due to common impurities, and that both O_2 and N_2 are necessary for its appearance. Measurements made on the arc facility with 60 Å resolution showed definite structure and indicate that the radiation is a compact molecular band. The arc and shock tube data can be correlated by assuming that the radiation originates from NO with an excitation energy of about 8 eV. Attempts to identify the band with a transition between known Rydberg states of NO were unsuccessful, but a possibility exists that the transition could occur because of an interaction between certain Rydberg and non-Rydberg states.

TABLE OF CONTENTS

I. INTRODUCTION

In a shock tube study on the "Continuum Infrared Radiation from High Temperature Air and Nitrogen," Taylor[1] found evidence of a band system in the region of 3.6 - 4.0μ, the source of which was unknown. In that study, the "4μ band" radiation was found to be about a factor of 2 above the background of the neutral Bremsstrahlung in air at 8000°K and a density of 0.9 STP. No spectral details were obtained nor was any attempt made to identify how the intensity scaled with the concentration of possible radiators in the high temperature air. Although Taylor speculated on the source of the 4μ radiation, it was concluded that more work was needed to establish its origin.

The present publication describes the results of an experimental program directed towards obtaining (1) high resolution spectra of the "4μ band," (2) the temperature dependence of its absolute intensity, and (3) its scaling with concentration of the components of high temperature air.

In order to accomplish this program, two different laboratory facilities were employed, i.e., a conventional shock tube and a one atmosphere arc jet. The shock tube yielded integral intensity measurements of the radiation from air behind the reflected shock covering a temperature range of approximately 6000 to 8000°K. Other gases were studied over a wider range of temperature. The arc facility gave both integral intensity measurements and high resolution ($\Delta\lambda$ = 60 Å, full width at half height) absolute intensity spectra around 6000°K.

The possibility that the source of the "4μ band" was an impurity was investigated in both facilities and it was shown that this was not the case. The high resolution spectra show considerable detail and rule out atomic line radiation and, in particular, sodium line radiation. Both the shock tube and arc data scale well with NO concentration, and, in the temperature region of overlap ($\sim$ 6000°K), the NO scaling accounts nicely for the factor of 70 in the absolute intensity between the two measurements.

II. EXPERIMENTAL TECHNIQUE

A. Arc

The arc facility used in these experiments has been described in detail in several previous publications.[2, 3, 4] The synthetic air (and other gases) exiting from the arc was shown to be in equilibrium in that earlier work. In the present study the 1.9 cm diameter exit nozzle was used, and the radiation was monitored within a few mm of the exit plane. The temperature of the arc heated gases is calculated from the arc energy balance assuming the gas to be in equilibrium.

The arc and associated optical system is shown in a highly schematic diagram in Fig. 1. The basic external optical system consisted of two 45° mirrors and a 24 inch focal length spherical mirror, the magnification of this system being unity.

A Perkin-Elmer Model #98 monochromator was used as a dispersion instrument; a motor drive enabled wavelength scans to be made. The radiation from the arc was chopped at about 1,000 cps just before entering the instrument. The dispersed radiation exiting from the instrument was detected with a liquid nitrogen cooled indium antimonide cell, the output of which was passed through a narrow band pass filter (General Radio Wave Analyzer Model 1900-A) centered at the chopping frequency before being recorded on one beam of an oscilloscope. The electronics were such that the sensitivity of the system was limited by cell noise. Both D.C. and A.C. (100 KC carrier wave) outputs from the General Radio filter were used.

The wavelength calibration of the instrument was obtained between 1 and 5.5μ (the entire range of sensitivity of the detector) using numerous IR standard absorption bands. A wavelength calibration signal was generated during the actual runs by means of a battery and variable resistor which was rotated by the motor drive. This calibration signal was displayed simultaneously with the radiation signal on the dual beam oscilloscope. For the high resolution spectra, a precise wavelength calibration was made employing an absorption cell containing HBr, which has 6 rotational lines between 3.934 and 4.078μ in its fundamental vibration-rotation band.[5] Absolute intensity calibration of the entire optical system and detector was accomplished with a blackbody source at 500°C. The monochromator has equal entrance and exit slits which, of course, yield a triangular wavelength resolution function. The theoretical half width $\Delta\lambda$, of this resolution for the calcium fluoride optics used has been given by Streiff and Ferriso.[6] Experimental verification of the theoretical resolution function was carried out using several atomic lines in the IR. For the low resolution runs, the slit width was 0.5 mm (slit height = 3.5 mm) which corresponds to $\Delta\lambda$ = 600 Å. A 1 rpm motor was used to drive the wavelength scan, it taking

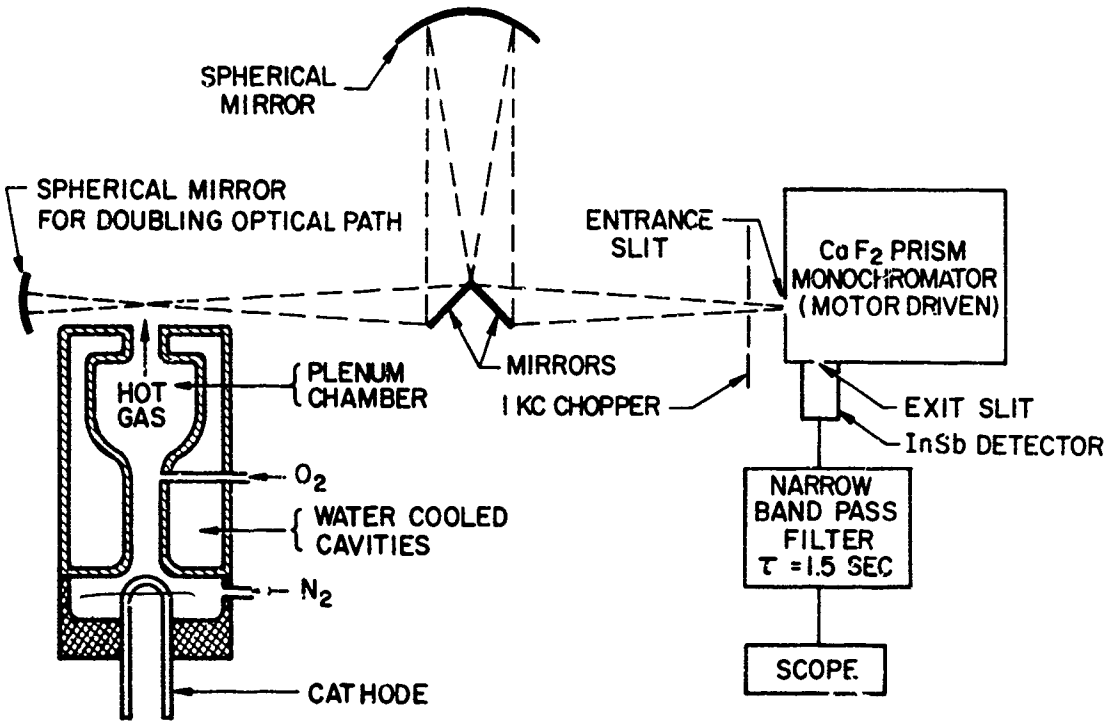

Fig. 1 Schematic diagram of arc and associated optical system used to obtain high wavelength resolution spectra.

A7816

about 45 sec to scan from $\lambda = 3.80$ to 4.15μ. The high resolution runs, made only at the highest temperatures where there was sufficient intensity, were made using a slit width of 0.05 mm yielding a $\Delta\lambda = 60$ Å. In order to obtain an adequate signal to noise ratio with the narrow slit, the slit height was increased to 12 mm, and a concave mirror for doubling the optical path was placed on the far side of the nozzle (see Fig. 1). Furthermore, the scanning motor speed was reduced to 0.1 rpm, it taking about 200 sec to scan from $\lambda = 3.92$ to 4.09μ. These high resolution runs employed the D.C. output from the General Radio filter and the signal was averaged with an integrating circuit with an RC = 1.5 sec before display on the oscilloscope.

To investigate the effects of metal impurities, water solutions of the nitrate salts of various metals including Cu, Ca, Sr, K and Na were injected into the arc heated air at the entrance to the arc plenum chamber. The H_2O amounted to 1% of the flow and the metal concentrations were about 0.1 mole % of the total air flow. Wavelength scans were made of the 4μ region simultaneously with constant solution injection.

To find out whether the 4μ radiation emanated from the free stream as opposed to the outer edge of the arc heated gas (i.e., the boundary layer originating on the copper nozzle), a few experiments were carried out using a scanning slit technique.[7] For this part of the study, a rectangular nozzle (1/2" high, 1" wide) was employed and a narrow, horizontal, motor driven slit was located between the monochromator entrance slit and the 1 kc chopper. The monochromator was set for 4μ and the slits were opened so that the band pass encompassed the whole 4μ band. The image of the driven slit was perpendicular to the entrance slit image and during a run it scanned vertically. Thus, as a function of time, the detector first saw the 4μ radiation emanating from the 1" long boundary layer on the bottom of the nozzle followed by the thin boundary layer on both sides of the nozzle plus the free stream.

B. Shock Tube

The shock tube used in this experiment and the associated optical instrumentation are described in detail in Ref. 8. The shock tube was of conventional design and has a total length of 12 feet. The low pressure section was terminated by a 1-ft-long square test section of inner dimension 1.38 inches. The test section was joined to the rest of the shock tube through a 1-ft-long constant area transition section. The remainder of the shock tube was of cylindrical cross section, 1.5 inches in diameter. The entire shock tube was constructed of stainless steel except for the aluminum test section.

To generate shocks either pressure breaks or, for the higher temperatures, combustion driving were used to rupture the diaphragm. The measurements were made behind the reflected shock, and the conditions of the shock heated gas were determined by measuring the incident shock velocity and assuming that equilibrium prevailed behind the reflected shock.

For the conditions discussed in this study the equilibrium assumption has been shown to be reasonable.[8] The incident shock velocity was measured by a set of 6 thin-film heat transfer gauges placed at intervals along the shock tube.

The square test section was used to facilitate the mounting of two plane, sapphire windows at opposite sides of the tube. The windows were 0.75-in-diameter and 0.040-in-thick and were positioned so that the center line of each window was 0.24 inches from the end plate of the tube.

The radiation behind the reflected shock was scanned in the vicinity of 4.0μ using a synchronized, high speed, scanning spectrometer described in detail in Ref. 9. A reflective optical system imaged radiation from the shock heated gas onto the entrance slit of this spectrometer. The scanning is achieved by means of a magnetically rotated mirror which sweeps the dispersed radiation over the exit slit of the spectrometer. The mirror can be accelerated to a constant velocity in 15-μsec, and the scan can be synchronized with the passage of the shock by the viewing station. The spectrometer scans 0.02 μ/μsec with a spectral resolution of 0.07μ (full width at half height). The radiation is detected at the exit slit with a liquid nitrogen cooled, indium antimonide detector.

The position of the scanning mirror is monitored by an independent optical system which reflects off the back side of the mirror. This monitor signal is displayed simultaneously with the signal from the infrared detector on a dual beam oscilloscope and provides an internal wavelength calibration on each run.[9]

To determine the absolute intensity of the continum radiation, the spectrometer was calibrated against a blackbody source. The calibration was carried out in the same geometric arrangement as used to obtain shock tube data, the source replacing the radiating gas. To minimize atmospheric absorption due to CO_2 or H_2O vapor, the end of the shock tube, the spectrometer, and the optics were enclosed in a box and purged with dry N_2. The absolute calibration is believed accurate to within 5-10 %. The wavelength calibration of the spectrometer was determined by scanning known sources in absorption and is believed known to within $\pm$ 0.01μ.[9]

The air used in this experiment was prepared by mixing O_2 and N_2 in the ratio of 1:4. The N_2 used was Matheson prepurified grade claimed by the manufacturer to contain 2 ppm of O_2 as the only impurity. The O_2 was Matheson extra dry grade stated to be 99.6% O_2 with no specification of impurity content. The Ne, Ar, and Xe were research grade gases stated to have the following minimum purities: Ne - 99.9993%; Ar - 99.998%; and Xe - 99.995%.

Before each run the shock tube was evacuated to pressures less than 3×10^{-5} torr with measured leak rates of $0.2 - 1.0 \times 10^{-3}$ torr/min. The initial pressures of the test gases varied between 10 to 100 torr.

III. EXPERIMENTAL DATA

A. Arc

In Fig. 2 is shown a composite reduced wavelength scan made on arc heated air at T = 5760°K in which the complete region of sensitivity of the InSb detector was explored in several runs. The slit width was 0.5 mm. It was in runs such as this that the "4μ band" was rediscovered on the arc facility. These runs were made with synthetic air (just N_2 and O_2 in the appropriate ratio); the CO_2 radiation observed in the vicinity of 4.3μ is due to entrained CO_2 from the ambient atmosphere. The entrainment of CO_2 (and other ambient impurities) could be made negligible by bleeding in an inert buffer gas (Ar, He, N_2) symmetrically from a ring surrounding the exit nozzle. This technique eliminated the 4.3μ CO_2 radiation but left the "4.0μ band" unchanged. Other features of interest are identified in Fig. 2, and a theoretical Bremsstrahlung calculation is shown for comparison. This calculation uses the effective Z^2 for neutral Bremsstrahlung from O, N and N_2 as a function of wavelength given by Taylor and Caledonia.[10]

In Fig. 3a is shown a typical oscillogram for a high resolution run. The D. C. display mode was used. The temperature for this run was 5790°K. The wavelength calibration used for the high resolution runs is shown in Fig. 3b. Seven such high resolution runs were made between 5500 and 5800°K.

As indicated above, runs were made with injected impurities to investigate possible impurity sources of the "4μ band." Because of its common occurrence as an impurity and the coincidence of several of its lines with the 4μ band region, one strong possibility was sodium. In Figs. 3c and d are shown high resolution spectra (A. C. mode) of synthetic air and synthetic air plus 0.1% Na. The Na contaminated run clearly shows the expected[11] Na lines at 3.986 and 4.046 μ, but no enhancement of the "4.0μ band." Similar runs were made with solutions of the nitrates of Cu, Ca, Sr, and K.

B. Shock Tube

Typical data obtained behind reflected shocks in air and N_2 with the high speed scanning spectrometer are shown in Fig. 4a and 4b respectively. Here, as in all the shock tube work, the spectral resolution was 700 Å (full width at half height). In both sets of oscillograms the top trace is the infrared signal from the scanning spectrometer, the middle trace is from the wavelength signal generator (from which the wavelength scale immediately below has been constructed), and the bottom scale is the monitor PM signal which indicates the uniformity of the test gas.

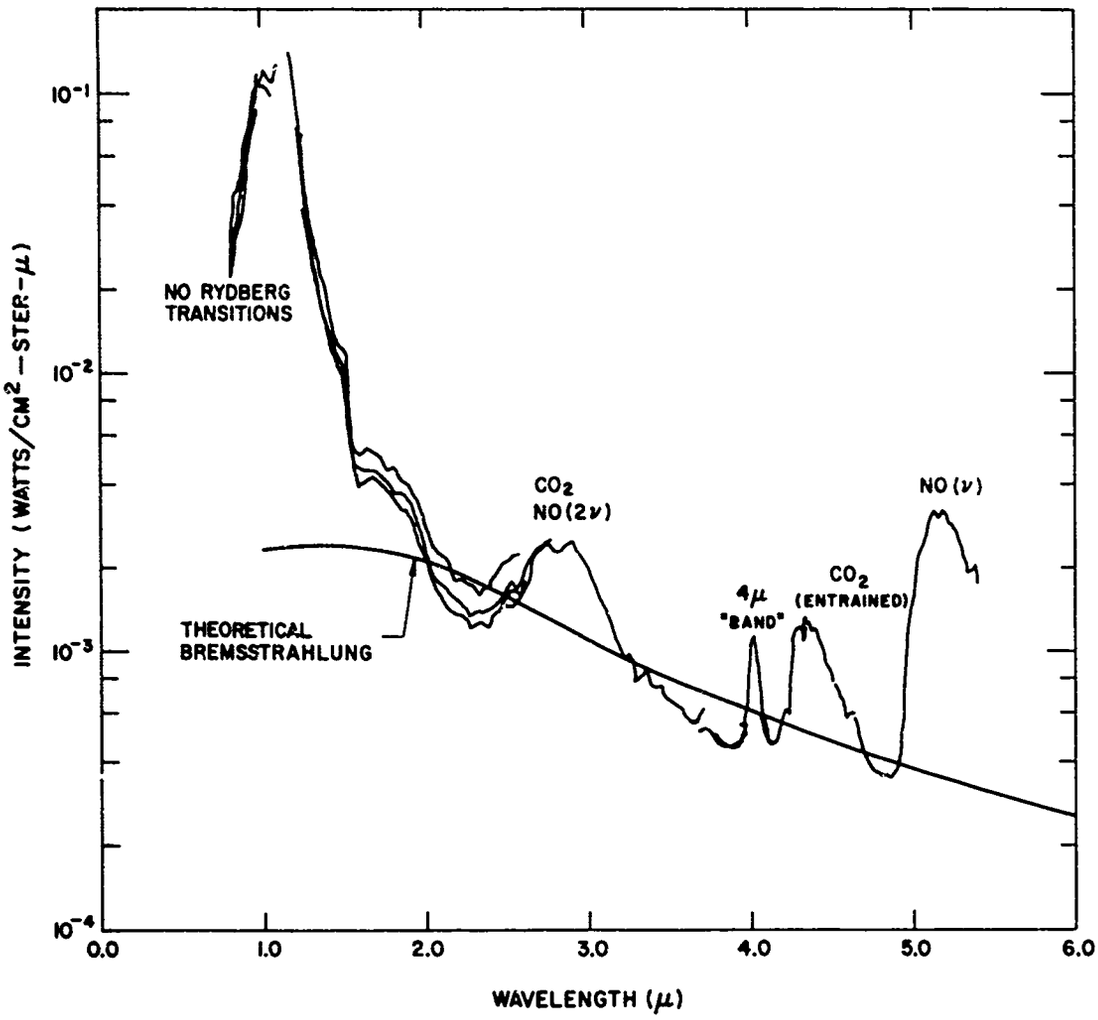

Fig. 2 Absolute radiation intensity of arc heated air plotted versus wavelength in the near IR. The arc energy balance temperature was 5760°K and the optical path length was 19 mm. Resolution in the vicinity of 4 μ was 600 Å. The theoretical Bremsstrahlung calculation is based on the experiments of Ref. 10.

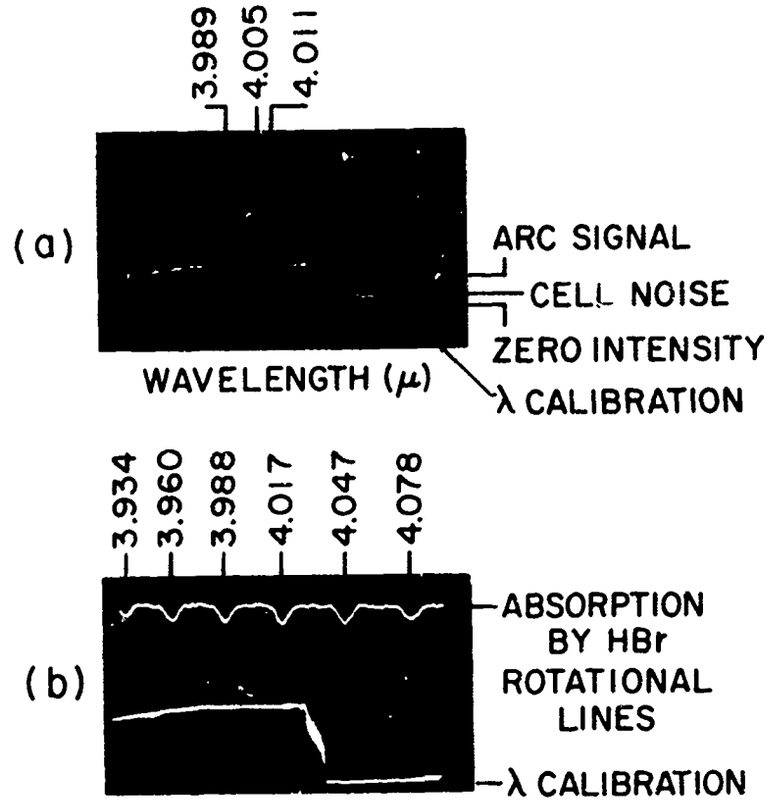

Fig. 3 (a) Typical high resolution oscillogram (D. C. display mode) T = 5790°K. Resolution = 60 Å (full width at half height).

(b) Wavelength calibration used for high resolution runs.

A7571

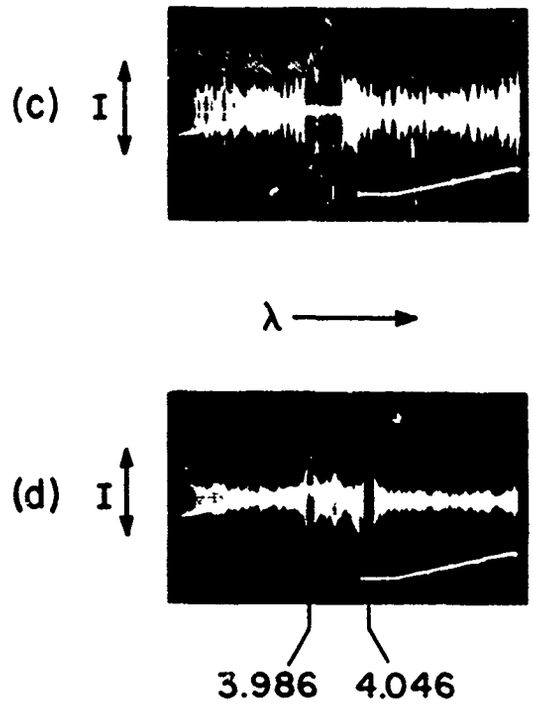

Fig. 3 (c) High resolution air spectrum (A. C. mode). Gain = 1.
(d) Air + 0.1% Na. Gain = 1/3.

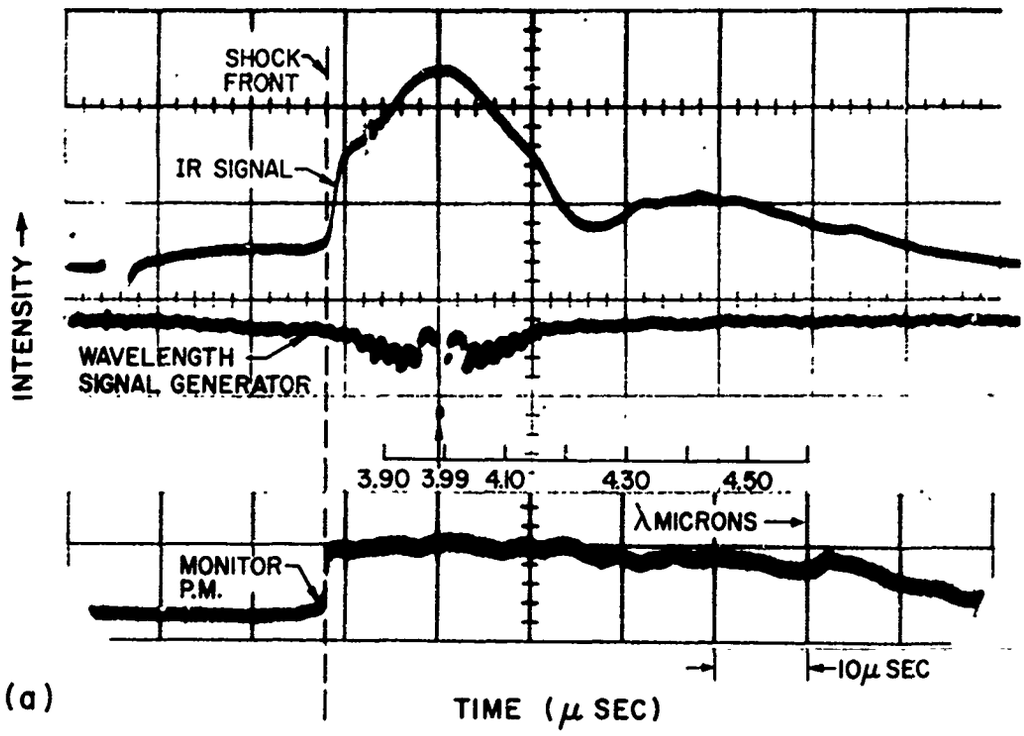

Fig. 4 (a) Typical data obtained behind reflected shock wave in air. P_1 = 10 torr, U_s = 4.52 mm/μ sec. T_4 = 7970°K.

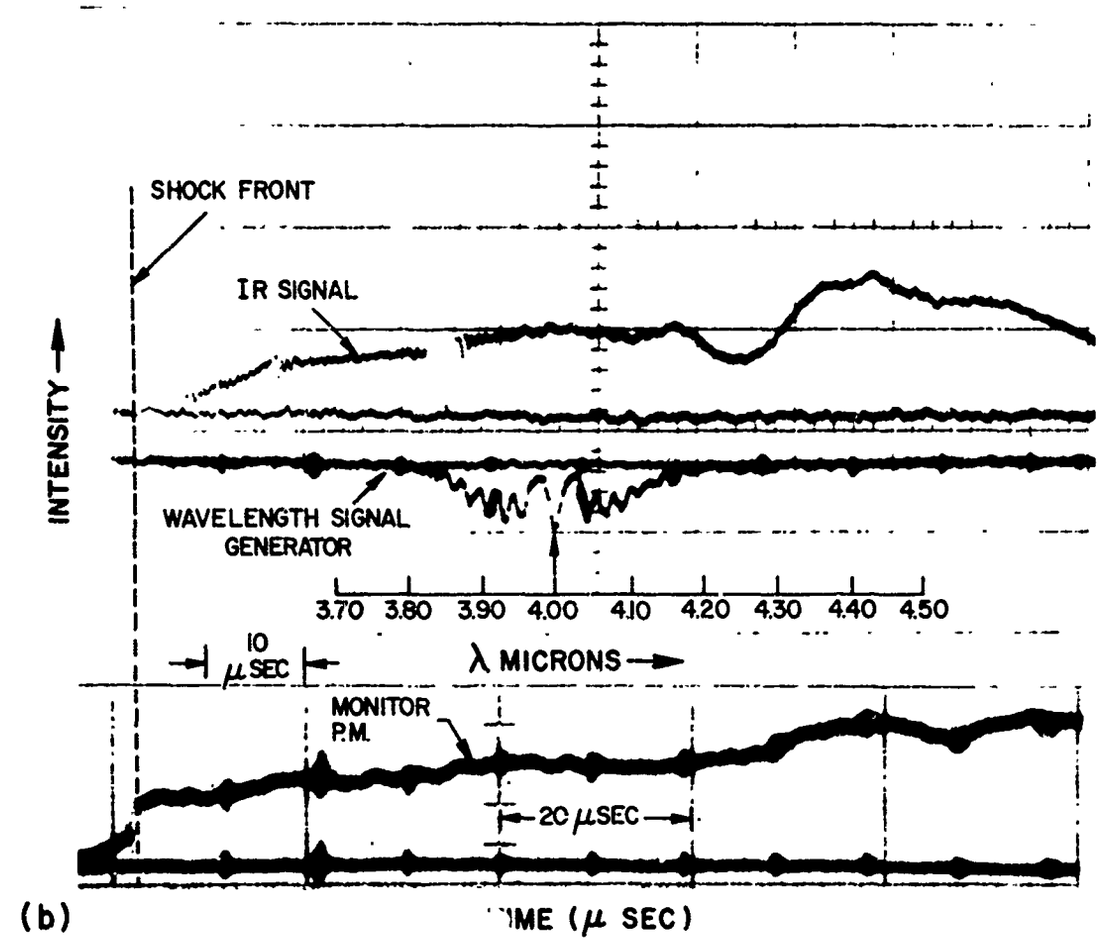

Fig. 4 (b) Typical data obtained behind reflected shock wave in nitrogen. P_1 = 10 torr, U_s = 3.76 mm/μ sec, T_4 = 7220°K.

As can be seen by comparing the top traces in 4a and 4b, the air exhibits a 4.0μ band while the N_2 does not. Atmospheric CO_2 absorption can also be seen at 4.26μ. In these experiments room air had not been completely purged from the optical system. Similar data were also obtained for Ne, Ar, Xe, and Ne-O_2 mixtures. In Ne at temperatures between 7000-10,000°K lines or groups of lines were observed at 3.89 $\pm$ 0.003 and 4.16 $\pm$ 0.004μ. At T = 10,000 to 16,000°K, besides the two original lines, a third feature arose centered at 4.00μ. In the 20% O_2 - 80% Ne mixture at T = 7000-10,000°K only one feature was apparent with a peak wavelength of 4.03 $\pm$ 0.01μ. In Xe from 7900-9100°K a feature was apparent at 3.90μ with no line at 4.00μ. Ar presented an interesting case since at all temperatures studied, T = 8100-12,000°K, there was a strong line(s) apparent at 4.00 $\pm$ 0.006μ.

In a few experiments small amounts of H_2 or C_2H_2 were added to the test gases with no noticeable change or enhancement of any of the features in the vicinity of 4.0μ. Also for air, N_2, and Ar a drum camera spectrograph was used to look for the Na resonance doublet at 5890 and 5896 Å. As expected, Na emission was observed. Using the spectrometer as a monochromator, the absolute intensity of the Na resonance line was measured, and an estimate of the neutral Na concentration in the gas obtained.

IV. DATA ANALYSIS

The scanning slit runs made with the rectangular nozzle showed a continuous rise of radiation through the nozzle boundary layer followed by a constant radiation level through the free stream. This indicated that the 4μ radiation came from the main body of the arc heated air and not from the boundary layer. In the shock tube it was found that the time dependence of the 4μ radiation was the same as the neutral Bremsstrahlung which suggests that here too the radiation eminated from the bulk gas.

The shock tube study of the sodium D line intensity yielded an estimate of the Na concentration. This estimate can vary considerably depending upon the temperature assumed for the radiating sodium, i.e., whether the sodium is assumed to be radiating from the free stream or the boundary layer. However, if the same temperature is used for determining both the sodium concentration from the resonance emission and the f-number of the 4μ radiator, then the f-number deduced for the latter is much greater than unity. Alternatively, this means that much more sodium is necessary to account for the 4μ radiation than is in agreement with the sodium resonance line emission intensity. In any case, the high resolution spectra of Figs. 3c and 3d demonstrate beyond any doubt that the 4μ band is distinctly different from the Na line emission. Similarly, potassium shows the 4.012μ line and the group of lines around 3.73μ as expected from the literature.[11] The potassium radiation at 3.73μ is not seen in the "clean" air. In total, these experiments rule out the metalic impurity hypothesis for the 4.0μ emission.

The shock tube data on the various gases add further substantiation to the conclusion that the 4.0μ radiation in air is not due to some universal impurity. The data on N_2 (see Fig. 4b), Xe, low temperature Ne, and the 20% O_2 - 80% Ne mixture show no 4.00μ radiation. However, Ne at temperatures above $10,000^{\circ}K$, and Ar do show anomalous radiation at about 4.00μ. It is believed that all of the features observed in the noble gases in the vicinity of 4.0μ are due to line radiation occurring between excited states lying close to the ionization limit of the neutral atom. Infrared lines in the noble gases have been previously observed[12] and Ne and Xe have been made to lase in the vicinity of 4.0μ in an electrical discharge.[13]

To check the possibility that the 4.00μ radiation might be due to lines, calculations were performed for the conditions of the Ar and Ne experiments. These calculations used appropriate energy levels close to the ionization limit of these atoms that were separated by 4.0μ. An f-number of 1.0 was also assumed. The calculations used the path length of the experiment and took account of the optical thickness. Both electron and neutral broadening mechanisms were estimated according to the method of Griem.[14]

Because of the various assumptions these calculations can only be considered approximate. However, the comparison with the data was fairly good both in terms of absolute magnitude and in terms of temperature dependence of the radiation. The Ne calculations indicated that the line radiation should be optically thin while that from the Ar was becoming black at the higher temperatures. The general agreement of the calculations and data support the belief that the radiation observed in the case of Ne and Ar at 4.0μ is due to highly allowed line radiation originating from closely spaced excited states lying near the ionization limit.

An example of the highest resolution 4μ spectral scan data was shown in Fig. 3a along with a wavelength calibration accomplished by scanning the absorption spectra of HBr (Fig. 3b). Seven runs, all at relatively high temperature, similar to that shown in Fig. 3a were made. Smooth curves were drawn through the oscilloscope traces consistent with the instrument resolution, and, with the aid of black body intensity calibrations and the HBr wavelength calibration, the data were reduced so as to produce absolute intensity versus wavelength plots, such as is shown in Fig. 5. The features shown in this spectrum are highly reproducible except that identified in Fig. 5 as λ_8 which is in the noise and is not clearly present in all the runs. In Table I the spectral features indicated in Fig. 5 are tabulated for all seven runs.

The discussion given above clearly rules out common metal impurities as a source of the 4μ radiation in air; also, as indicated above, traces of CO_2 or H_2O cannot be its source. Furthermore, the shock tube data show that neither N_2 nor O_2 by themselves yield the 4μ band. The high resolution spectra taken in the arc are highly indicative but, of course, do not absolutely prove, that the 4μ radiation is indeed a "band" as opposed to atomic line radiation. Hence, we are led to believe that this radiation emanates from the NO molecule, a significant component of equilibrium high temperature air.

To test this hypothesis the integrated absolute intensity of the 4.0μ radiation in air obtained on the arc from 5400 to 5800°K and on the shock tube from 6000 to 8000°K have been scaled by the NO particle density and plotted together on an Arrhenius plot as shown in Fig. 6. This scaling correlates both sets of data and produces a reasonable straight line over the entire temperature range. At 6000°K, which is the lowest temperature shock tube data and the highest temperature arc data, the NO scaling properly adjusts a factor of 70 in the ratio of absolute intensities obtained from the two experimental techniques. The shock tube data treated by itself yields a least squares slope activation energy of 7.8 eV.

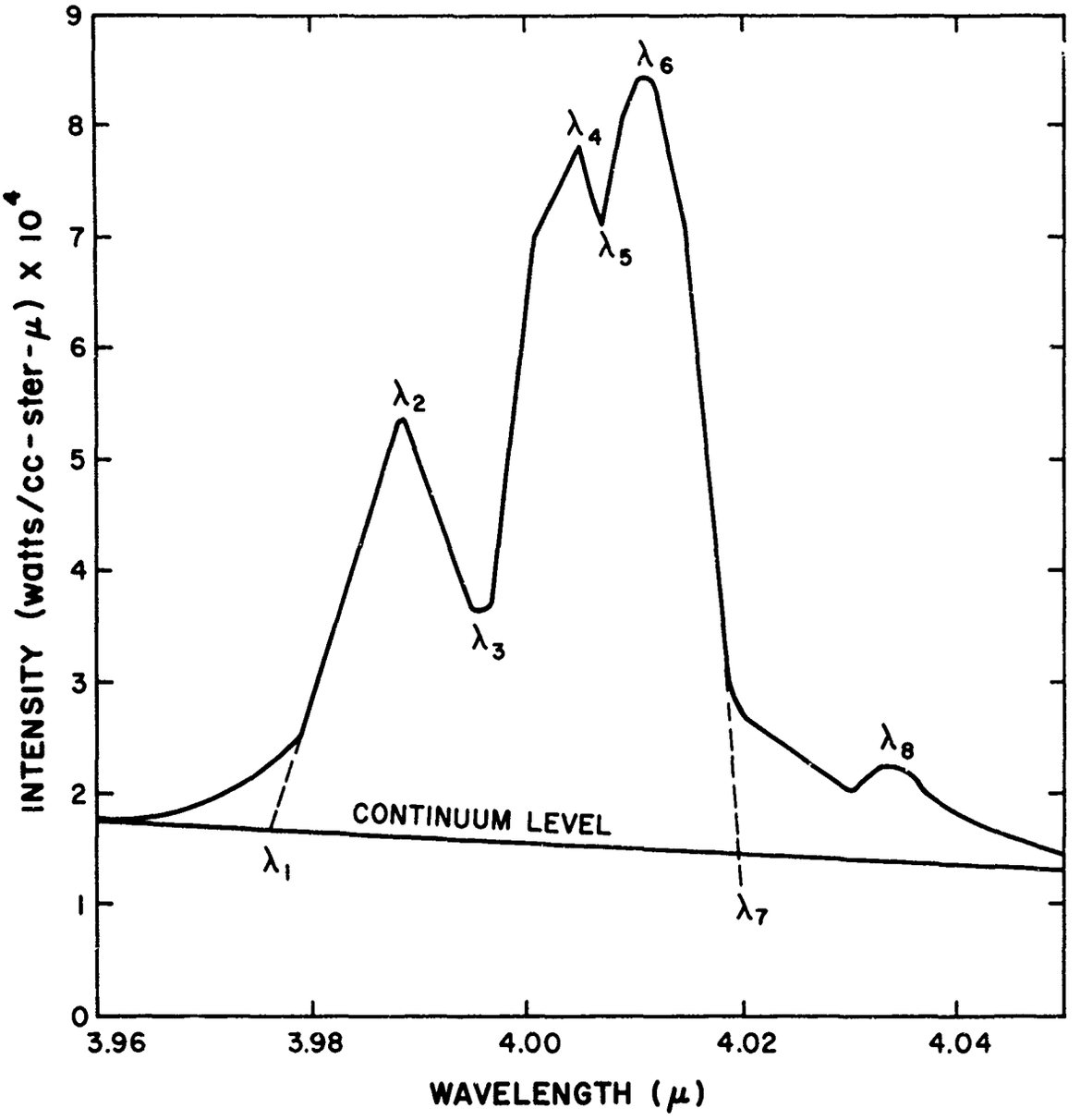

Fig. 5 Absolute intensity plotted versus wavelength. T = 5790°K. This spectrum was obtained from the oscillogram shown in Fig. 3(a). The wavelengths λ_1 through λ_8 are tabulated for seven runs in Table I.

A8326

TABLE I

Wavelength (in Angstroms) of Spectral Features of "4μ Band" Radiation from High Temperature Air (See Fig. 5 for λ Notation)

Run	T	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7	λ_8
1	5620	39855	39905	39972	40060	40072	40149	40200	40450
2	5510	-	39955	39985	40054	40075	40145	40223	40310
3	5730	39764	39922	39970	40050	40060	40095	40212	-
4	5710	39817	39906	39967	40055	40067	40139	40221	40370
5	5790	39761	39885	39950	40050	40070	40108	40196	40340
6	5790	39791	39915	39963	40046	40060	40130	40238	40370
7	5725	39813	39913	39990	-	-	40122	40222	40330
Avg.		39800	39914	39971	40052	40067	40127	40216	40362
Avg. Dev.		± 28	± 14	± 9.7	± 3.8	± 5.7	± 16	± 11	± 35

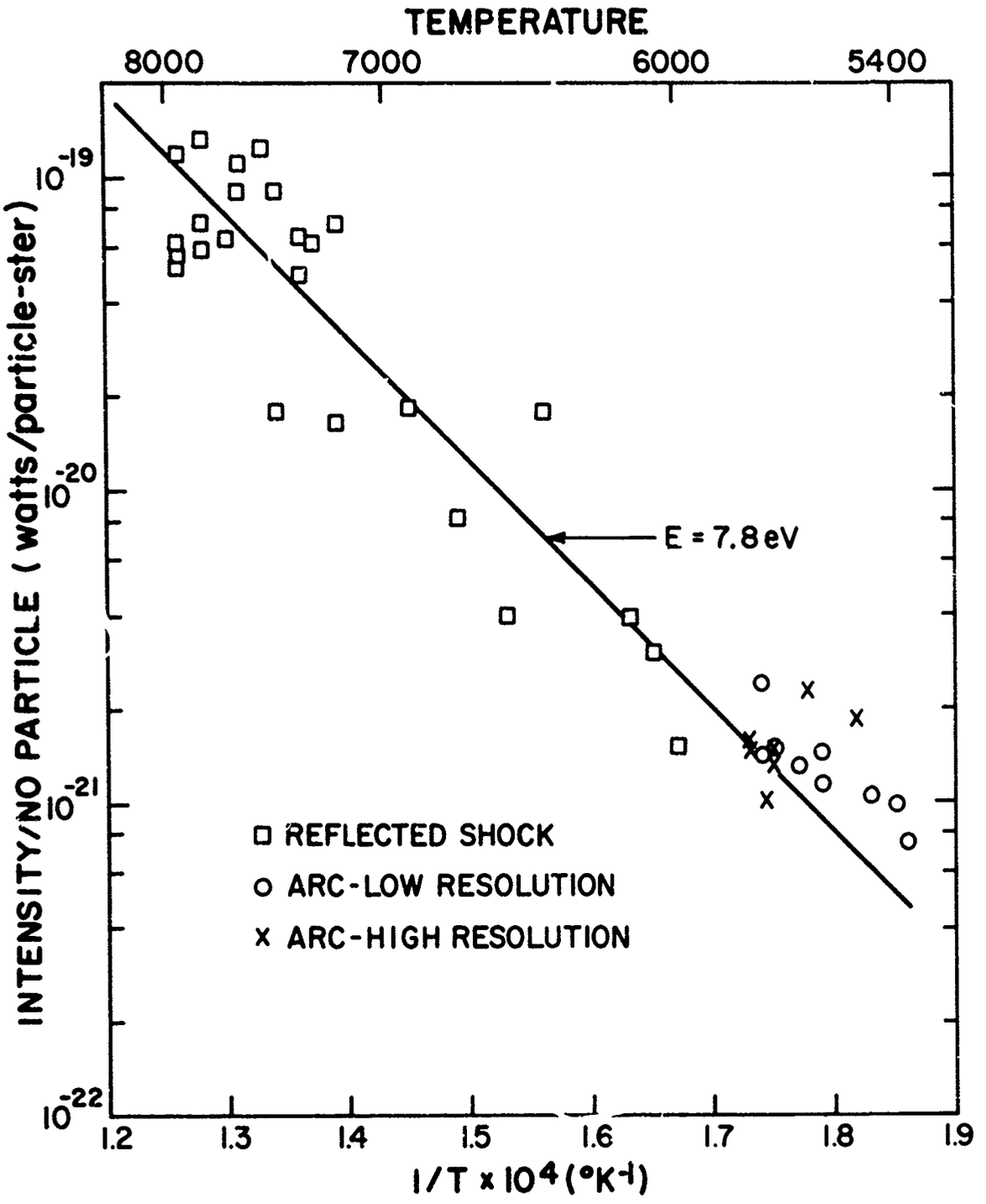

Fig. 6 Arrhenius plot of the radiation in the 4 μ band divided by nitric oxide concentration. Both the shock tube and the arc data are shown.

V. THEORY

As indicated above, it seems likely that the 4μ band of radiation in high temperature air is due to molecular radiation from NO. A potential energy diagram for nitric oxide has been prepared by Gilmore[15] and is reproduced in part in Fig. 7. During the progress of the present experimental work, it was considered possible that the 4μ band originated from a radiative transition between two Rydberg states of NO. The reason for this was that some of these transitions tend to have a high f-number and a narrow wavelength extent[4], both of these properties being exhibited by the 4μ band. The computed wavelengths of the band origins for the 0, 0 transitions between the ten lowest lying Rydberg states of NO are given in Ref. 4 (Table II). Of the 45 conceivable transitions, 10 fall within the range $2.5 \leq \lambda \leq 5.5\mu$. One of these cases, $M^2\Sigma \rightarrow F^2\Delta$ (band origin $\lambda = 3.834\mu$), has $\Delta\Lambda = 2$ which is a forbidden transition for Hund's case b. $^2\Sigma^+$ states are always case b and the $F^2\Delta$ state is believed to be near case b.[16] Hence, this transition was not considered as a possible source of the 4μ radiation.

For the remaining 9 possible transitions (H $\rightarrow$ E, H' $\rightarrow$ E, K $\rightarrow$ E, M $\rightarrow$ E, K $\rightarrow$ F, M $\rightarrow$ H, M $\rightarrow$ H', S $\rightarrow$ K, and S $\rightarrow$ M), detailed spectral computations were carried out at 5700°K using the theoretical model given in detail in Ref. 4. These were line by line computer calculations carrying rotational quantum numbers J up to 200. Only the 0, 0 and 1, 1 bands were considered; the Franck-Condon factors $q_{v'v''}$ were set equal to unity. The lines were summed in intervals of 60 Å corresponding to the high resolution experiments.

The results of these calculations were that only the $S^2\Sigma^+ \rightarrow M^2\Sigma^+$ transition could possibly be responsible for the 4μ radiation, the other 8 systems producing spectral shapes whose dominant features and their wavelengths were completely dissimilar to the experimental spectrum. The S $\rightarrow$ M calculated spectrum is shown in Fig. 8; comparison of it with the experimental spectrum of Fig. 5 shows that the two spectra are really quite dissimilar also. However, it should be pointed out that the exact wavelengths of the band heads R_{00} and R_{11} are very sensitive to the values of B_v for the two states involved. These spectroscopic parameters may not be known sufficiently well to definitely eliminate the S $\rightarrow$ M transition as the source of the 4μ band.

On the other hand, the S $\rightarrow$ M system interpretation of the data would demand an unacceptably large f-number. The synthetic spectrum of Fig. 8 assumes unit f-number. An experimental f-number can readily be deduced by comparing the $I/NO = 1.5 \times 10^{-21}$ watts/NO particle-ster from Fig. 6 with the computed integrated intensity of Fig. 8 which is 3.08×10^{-22}. After applying a correction factor of 1.48 for the effect of neglecting vibrational states of $v' \geq 2$, an effective absorption f-number of 3.3 is calculated.

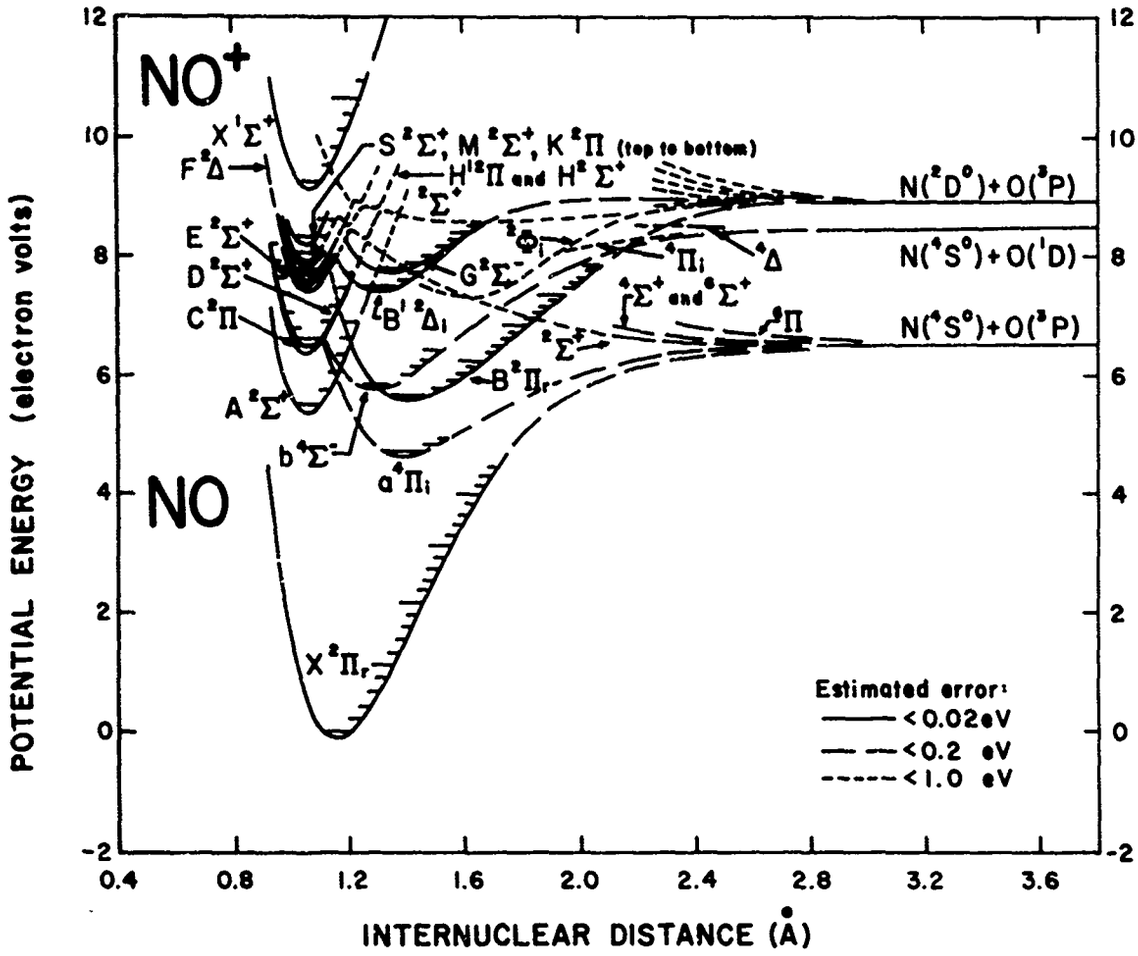

Fig. 7 Potential energy diagram for nitric oxide showing the various electronic states of interest in this study (from Ref. 15).

A7811

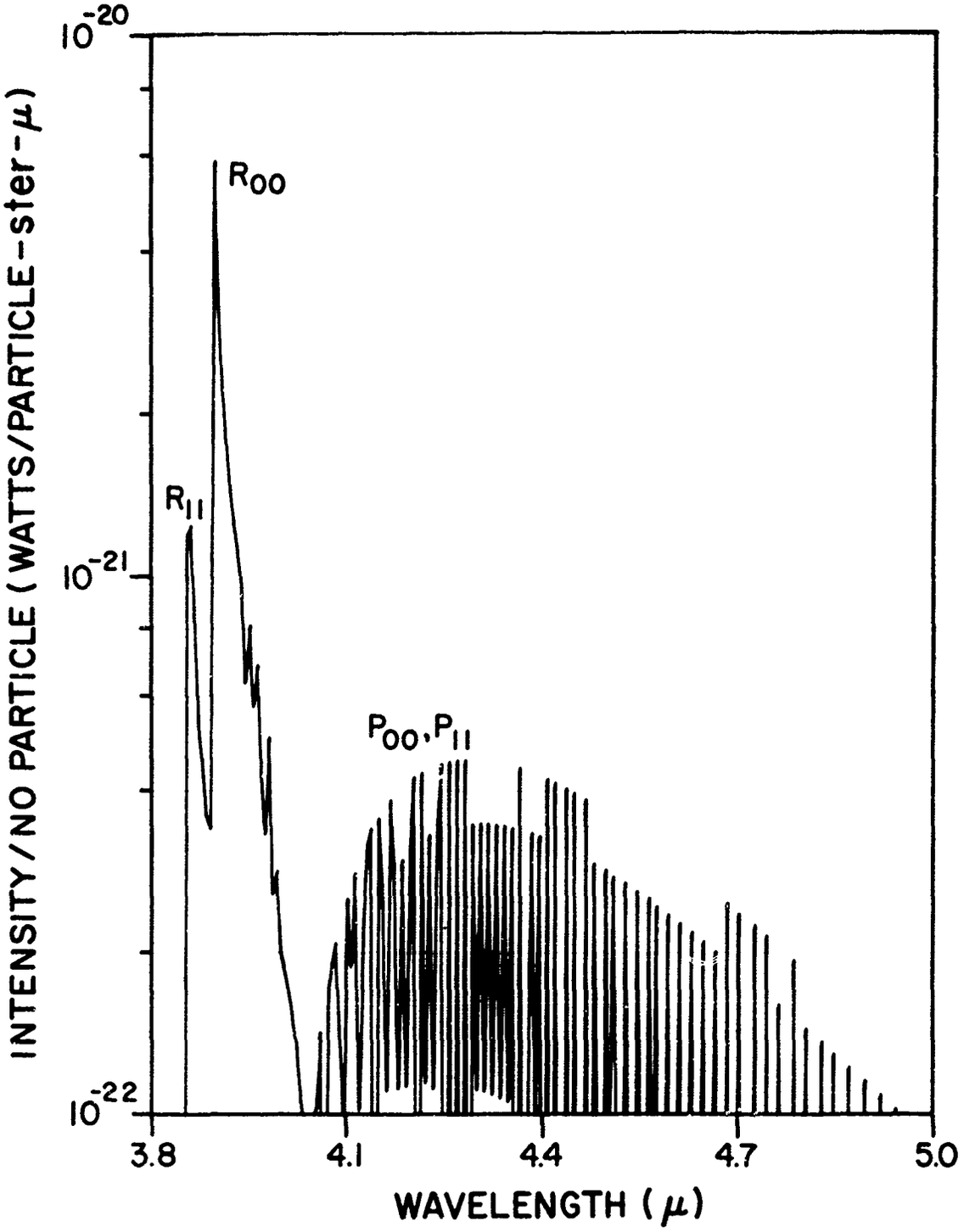

Fig. 8 Theoretical computed radiation intensity per particle as a function of wavelength for the nitric oxide Rydberg transition $S^2\Sigma^+ \rightarrow M^2\Sigma^+$ at T = 5700°K. The product of the Franck-Condon factor and the f-number was taken to be unity. Only (0, 0) and (1, 1) bands were included. The P and R branches are indicated; only the R branches form heads.

Another possible explanation of the 4μ radiation is a transition between Rydberg and non-Rydberg states of NO similar to the well known $B'^2\Delta \rightarrow C^2\Pi(4,1)$ system.[17] There are ample possibilities for such to exist, i.e., it has been pointed out that the non-Rydberg states B'(v=6) and L(v=2) interact with the Rydberg states F(v=2) and K(v=0), respectively.[18] Hence, transitions $B' \rightarrow K(6,0)$ and $F \rightarrow L(2,2)$ are possible and, furthermore, the energies are such that the radiation would occur at about 4μ.

VI. SUMMARY AND CONCLUSIONS

In the present work it has been shown that the 4μ band of radiation from hot air in both the arc and shock tube cases is indeed attributable to a component of high temperature air. The impurity hypotheses has been explored in depth and has proved negative. The high resolution data strongly suggest a compact band system. The shock tube and arc data scale well with nitric oxide concentration and indicate an excited state lying about 8 eV above the ground NO state.

Rydberg-Rydberg transitions were considered as possible sources but the results of detailed synthetic spectra calculations were mostly negative with just an outside chance that the source of radiation is due to the $S^2\Sigma^+ \rightarrow M^2\Sigma^+$ system. More likely, however, the 4μ band radiation is due to a non-Rydberg $\leftrightarrow$ Rydberg transition.

VII. ACKNOWLEDGMENTS

The authors wish to acknowledge the aid given by Messrs. H. Koritz and E. Feldman in running the arc facility and by Mr. C. Deradourian in running the shock tube. Also, we thank Mr. P. MacLean for carrying out the many computer calculations of the theoretical spectra.

REFERENCES

1. Taylor, R. L., J. Chem. Phys. 39, 2354 (1963).

2. Wray, K. L., Rose, P. H., and Koritz, H. E., "Measurements of the Radiation from an Ablation Contaminated Boundary Layer under Simulated Flight Conditions," Avco Everett Research Laboratory Research Report 226 (August 1965).

3. Wray, K. L., and Kemp., N. H. AIAA 3rd Aerospace Sciences Meeting, January 24-26, 1966, New York, AIAA Paper No. 66-56.

4. Wray, K. L., "Oscillator Strengths of Transitions between Rydberg States of Nitric Oxide in the Near IR," Avco Everett Research Laboratory Research Report 300, (August 1968), accepted for publication in J. Q. S. R. T.

5. Plyler, E. K., Danti, A., Blaine, L. R., and Tidwell, E. D., J. of Research of the National Bureau of Standards -- A. Physics and Chemistry, Vol. 64, No. 1, January-February 1960.

6. Strieff, M. L., and Ferriso, C. C., "Spectral Slit Width of a Small Prism Monochromator," GDA-DBE64-054, General Dynamics/ Astronautics Space Science Laboratory, (August 1964).

7. Greenberg, R. A., Kemp, N. H. and Wray, K. L., "Structure of the Laminar Ablating Air-Teflon Boundary Layer," Avco Everett Research Laboratory Research Report 301 (November 1968).

8. Taylor, R. L. and Caledonia, G., "Experimental Determination of the Cross Section for Neutral Bremsstrahlung I. Ne, Ar, and Xe," Avco Everett Research Laboratory Research Report 311, (September 1968), accepted for publication in J. Q. S. R. T.

9. Camm, J. C., Taylor, R. L. and Lynch, R., Appl. Optics 6, 885 (1967).

10. Taylor, R. L. and Caledonia, G., "Experimental Determination of the Cross Sections for Neutral Bremsstrahlung II. High Temperature Air Species - O, N, and N_2," Avco Everett Research Laboratory Research Report 312, (September 1968), accepted for publication in J. Q. S. R. T.

11. Moore, C., Atomic Energy Levels, Vol. I, Circular of the National Bureau of Standards 467, June, 1949.

12. Rao, K. N., Humphrey, C. T. and Rank, D. H., Wavelength Standards in the Infrared (Academic Press, New York 1960).

13. Bennett, W.R., Jr., Appl. Optics Suppl. 2, 3 (1965).

14. Griem, H.R., Plasma Spectroscopy, (McGraw-Hill Book Co., New York, 1964).

15. Gilmore, F.R., Rand Memo RM-4034-PR (June 1964).

16. Lagerqvist, A., and Miescher, E., Can. J. Phys. 40, 352 (1962).

17. Huber, M., Helv. Phys. Acta. 37, 329 (1964).

18. Huber, M, private communication; November 1968.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) Avco Everett Research Laboratory 2385 Revere Beach Parkway Everett, Massachusetts	2a REPORT SECURITY CLASSIFICATION Unclassified 2b GROUP

3 REPORT TITLE

4 μ Band Radiation from High Temperature Air

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Research Report 322

5 AUTHOR(S) (Last name, first name, initial)

Wray, K. L. and Taylor, R. L.

6 REPORT DATE	7a TOTAL NO OF PAGES	7b NO. OF REFS
	30	18

8a CONTRACT OR GRANT NO F04701-68-C-0036 b PROJECT NO c d	9a ORIGINATOR'S REPORT NUMBER(S) Research Report 322 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report) SAMSO-TR-68-468

10 AVAILABILITY/LIMITATION NOTICES

Distribution of this document is unlimited. This indicates document has been cleared for public release by competent authority.

11 SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Advanced Research Projects Agency, Department of Defense, ARPA Order #1092 and SAMSO, AFSC, Deputy for Re-entry Systems (SMY), Norton Air Force Base, Cal. 92409.

13 ABSTRACT

Experimental measurements are reported on high temperature air and other gases to establish the source of a band of radiation observed at 4.0 μ. Both a 1 atm arc jet and a shock tube were used to provide a temperature range of 5400-8000°K in air. Experiments established that the radiation was not due to common impurities, and that both O_2 and N_2 are necessary for its appearance. Measurements made on the arc facility with 60 Å resolution showed definite structure and indicate that the radiation is a compact molecular band. The arc and shock tube data can be correlated by assuming that the radiation originates from NO with an excitation energy of about 8 eV. Attempts to identify the band with a transition between known Rydberg states of NO were unsuccessful, but a possibility exists that the transition could occur because of an interaction between certain Rydberg and non-Rydberg states.

DD FORM 1 JAN 64 1473

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) Avco Everett Research Laboratory 2385 Revere Beach Parkway Everett, Massachusetts	2a REPORT SECURITY CLASSIFICATION Unclassified 2b GROUP

3 REPORT TITLE

4 μ Band Radiation from High Temperature Air

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Research Report 322

5 AUTHOR(S) (Last name, first name, initial)

Wray, K. L. and Taylor, R. L.

6 REPORT DATE	7a TOTAL NO OF PAGES	7b. NO. OF REFS
	30	18

8a CONTRACT OR GRANT NO	9a ORIGINATOR'S REPORT NUMBER(S)
F04701-68-C-0036 b PROJECT NO c d	Research Report 322 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report) SAMSO-TR-68-468

10 AVAILABILITY/LIMITATION NOTICES

Distribution of this document is unlimited. This indicates document has been cleared for public release by competent authority.

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	Advanced Research Projects Agency, Department of Defense, ARPA Order #1092 and SAMSO, AFSC, Deputy for Re-entry Systems (SMY), Norton Air Force Base, Cal. 92409.

13 ABSTRACT

Experimental measurements are reported on high temperature air and other gases to establish the source of a band of radiation observed at 4.0 μ. Both a 1 atm arc jet and a shock tube were used to provide a temperature range of 5400-8000°K in air. Experiments established that the radiation was not due to common impurities, and that both O_2 and N_2 are necessary for its appearance. Measurements made on the arc facility with 60 Å resolution showed definite structure and indicate that the radiation is a compact molecular band. The arc and shock tube data can be correlated by assuming that the radiation originates from NO with an excitation energy of about 8 eV. Attempts to identify the band with a transition between known Rydberg states of NO were unsuccessful, but a possibility exists that the transition could occur because of an interaction between certain Rydberg and non-Rydberg states.

DD FORM 1 JAN 64 1473

UNCLASSIFIED

Security Classification